Recent Advances in Negative Ion Mass Spectrometry

by John H. Bowie*

The paper describes theoretical and applied applications of negative ion chemistry carried out at Adelaide during the past five years. Kinetic energy release in negative metastable ion decompositions is described, with particular reference to simple cleavage reactions, rearrangement reactions, and reactions which proceed by dual mechanisms. The application of deuterium isotope effects as a mechanistic probe is illustrated by reference to the elimination of ketene from quinone acetate negative ions.

Charge stripping of a negative ion yields a decomposing positive ion, which produces a dissociative charge inversion spectrum of the negative ion. This technique allows the study of positive ions not available by conventional ionization; it provides a fingerprint for the parent positive ion produced in the collision process, and it may be used to determine the structure of the precursor negative ion. Finally, a combination of a negative ion spectrum and a charge inversion spectrum may be used as an analytical technique for the structure determination of unknown molecules.

Introduction

This conference is primarily devoted to a discussion of the applied aspects of negative ion chemical ionization mass spectrometry. To complement this discussion I wish to review some of the more fundamental aspects of our recent studies of the reactivity of negative ions. I will cover three separate topics: (a) the application of kinetic energy release in negative metastable ion decompositions as a mechanistic probe, (b) deuterium isotope effects in negative metastable ion decompositions, and (c) collision-induced fragmentations of negative ions with particular reference to the charge stripping of negative ions to positive ions and the theoretical and applied application of the charge-stripping technique.

Molecular negative ions discussed in this paper are produced by the low-energy electron capture process, $AB + e^- \rightarrow AB^-$, and fragment negative ions are formed by the dissociative process $AB + e^- \rightarrow [AB^-]^* \rightarrow A^- + B$. In our studies, negative molecular ions are formed by capture of low-en-

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ergy secondary electrons, originating at either metal surfaces or from gas-phase positive ionization (i.e., $AB + e^- \rightarrow AB^+ + 2e^-$). Primary electron energies of 70 eV are used. An Hitachi Perkin-Elmer R.M.U.7D mass spectrometer was used to record all spectra.

A review of the formation of specific molecular anions, and of their unimolecular decompositions to fragment negative ions, is beyond the scope of this article; these aspects have been covered in earlier reviews (1-4). In brief, many aromatic and heterocyclic systems which contain at least one electron withdrawing substituent (e.g., NO_2, CN, CO_2H, etc.) (3, 5), and organometallic and inorganic compounds which have either vacant orbitals or a suitable ligand (2, 3), may capture low-energy electrons. Such compounds, at 40-80 eV, produce negative-ion currents which are at least comparable to the ion currents produced by the analogous positive ionization. Certain aliphatic compounds, particularly those containing halogen, sulfur, or phosphorus substituents, also yield negative ion mass spectra. Negative ion spectra are often at least as informative for structure determination as the corresponding positive ion spectra (1, 3).

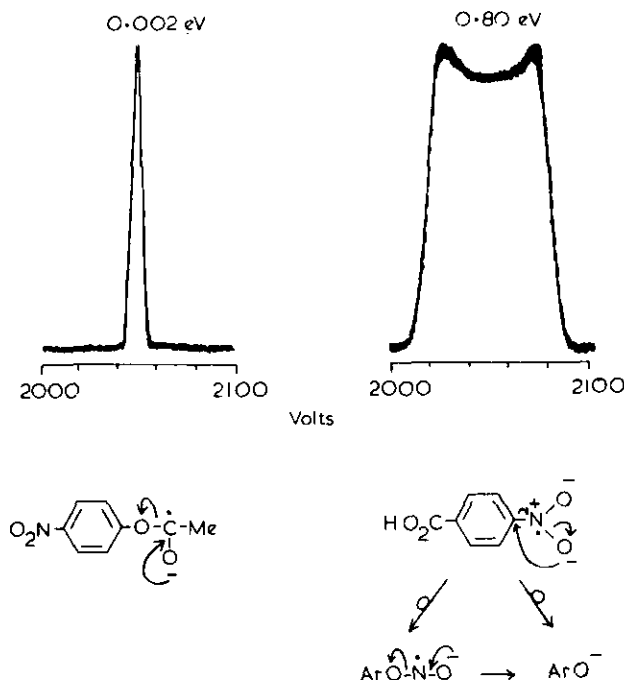O·OO2 eV   O·8O eV

2000   2100   2000   2100

Volts

FIGURE 1. Metastable peak profiles for (a) the loss of an acetyl radical from the p-nitrophenylacetate molecular negative ion and (b) the loss of NO from the p-nitrobenzoic acid molecular negative ion. Accelerating voltage scan.

Metastable Ion Studies

Kinetic Energy Release as a Mechanistic Probe

If an ion decomposes after acceleration in the analyser region of a mass spectrometer, the unimolecular reaction is called a metastable ion decomposition. Metastable decompositions are explicable in terms of the quasi-equilibrium theory of mass spectrometry (6), as occurring from low-energy precursor ions within a narrow energy region controlled by narrow rate constant limits (log $k \simeq$ 5-6). Parent negative ions, formed by secondary electron capture are produced with relatively low internal energies. As a consequence, negative ion spectra characteristically show much less fragmentation in the ion source than observed for a positive ion spectrum, but a corresponding increase in the abundance of peaks formed by metastable negative ion decompositions is noted. Another feature of negative ion spectra is that metastable ions formed by rearrangement processes are generally more prevalent and more abundant than those observed for simple bond cleavage (3). This is a direct consequence of the low internal energy of the decom-

posing negative ion (3, 6). The high abundance of negative metastable ions makes them particularly suitable for studies of the mechanisms of negative ion decompositions.

When a negative ion fragments unimolecularly, internal energy may be converted into kinetic energy of separation of the fragments (7). The shape of the resulting metastable peak, together with the value of the kinetic energy release T may be used as a convenient probe for mechanistic studies of negative ion reactions in the gas phase. A convenient measure of T is the kinetic energy peak width (7) at half height. Simple cleavage reactions of negative ions yield gaussian metastable peaks with small T-values, whereas rearrangement reactions give metastable peaks (either flat-topped or dish-shaped) with large T values (8-11). An example of a simple cleavage can be seen in Figure 1, where the loss of CH_3CO^- from the p-nitrophenyl acetate negative ion shows a gaussian metastable peak with T = 0.002 eV. The second metastable peak shown in Figure 1 is that for the loss of NO^- from p-nitrobenzoic acid. If this reaction is produced by the stepwise rearrangement shown in Figure 1 then the metastable peak will be sharp. If the rearrangement occurs by the alternative concerted reaction the peak will be broad. The T value of 0.80 eV is thus consistent with reaction by the latter process. (10).

In certain cases (10, 11) kinetic energy profiles of negative ion decompositions show composite peaks. This indicates that the process is occurring by more than one mechanism. Such a phenomenon, although relatively common for positive ion decompositions, is a rare occurrence for negative ions. Figure 2 shows a composite peak for the loss of NO^- from the m-nitrobenzoic acid molecular anion. A rationale for the two processes is shown in Figure 2 (10).
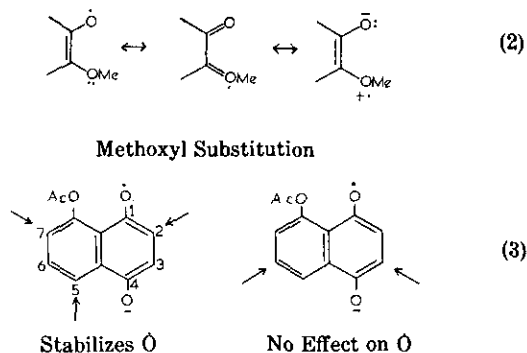
Deuterium Isotope Effects in Negative-Ion Metastable Decompositions

The application of isotope effects as a mechanistic aid for mass spectral processes has been very limited (12). We have found the kinetic isotope effect to be a powerful mechanistic probe for positive-ion decompositions (13), particularly when combined with theoretical calculations (14, 15). A deuterium isotope effect increases for a particular reaction as the internal energy of the decomposing ion decreases (i.e., as the lifetime of the ion increases). The value of the deuterium isotope effect for a metastable ion decomposition is

90

thus higher than that observed for a decomposition occurring in the ion source. Our kinetic isotope effects are therefore measured for negative ion metastable decompositions; usually those occurring in the first field-free region of the RMU 7D mass spectrometer (16, 17).

Proton Transfer   Hydrogen Atom Transfer

$$(1)$$
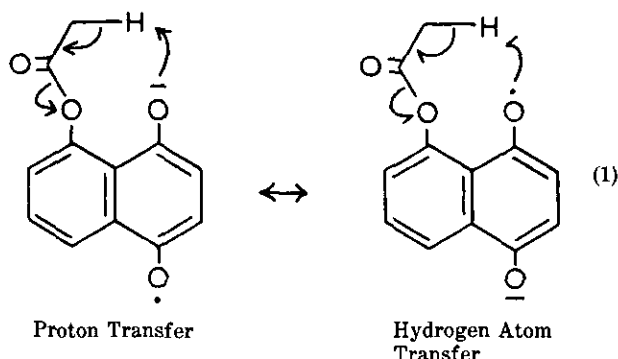
Let us consider a specific example of the use of kinetic isotope effects to give information about a transition state. If a negative ion contains an acetoxy substituent adjacent to a phenoxide site, hydrogen is transferred to the phenoxide site and ketene is eliminated (16, 17). The hydrogen transfer is involved in the rate determining step of the reaction, and the transition state is 'product like' according to the Hammond postulate (18). The isotope effect (k_H/k_D) for loss of CH_2CO from the 8-acetoxy-1,4-naphthoquinone molecular anion is 2.45. This example is shown in Eq. (1). The molecular anion can be drawn as two contributing structures. One shows an oxygen radical acceptor site (hydrogen ion transfer), the other a phenoxide anion acceptor site (proton transfer). It is of interest to speculate whether it is possible to differentiate between a "radical-like" and an "anion-like" reaction, and and whether isotope effects might help to solve this problem.

Methoxyl Substitution

Stabilizes Ȯ   No Effect on Ȯ

Let us assume that the reaction proceeds by a radical mechanism. If we are to use kinetic iso-

Volts

FIGURE 2. Composite metastable peak for the loss of NO from the m-nitrobenzoic acid molecular negative ion. Accelerating voltage scan.

tope effects to study this problem, we must introduce a substituent into the system which will affect the isotope effect by stabilizing (or destabilizing) a particular radical center without affecting the anion center. Methoxyl substituents are known (19) to stabilize phenoxide radical centres when the two groups are in conjugation. It has been suggested that such stabilization can be rationalized by the dipolar contributing structure shown in Eq. (2). If a methoxyl substituent is placed in the 2, 5, or 7 positions of the naphthoquinone ring Eq. (3), the radical center at position 1 will be stabilized. In these cases, the parent ion will be stabilized with respect to the transition
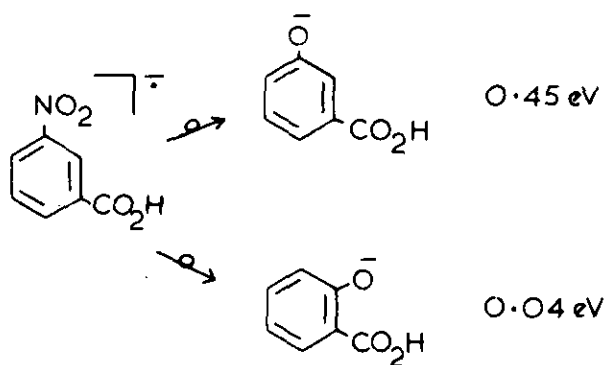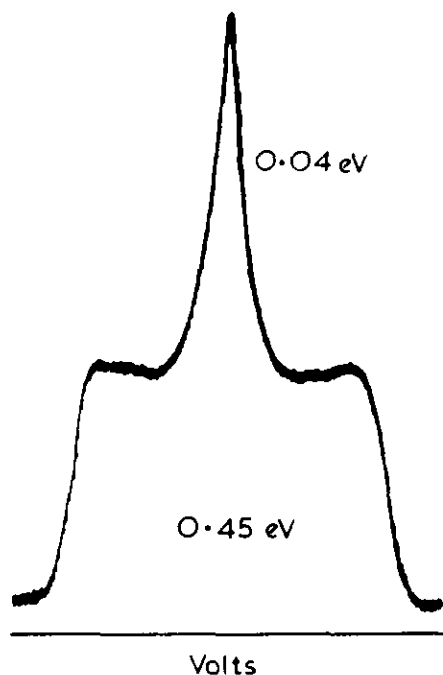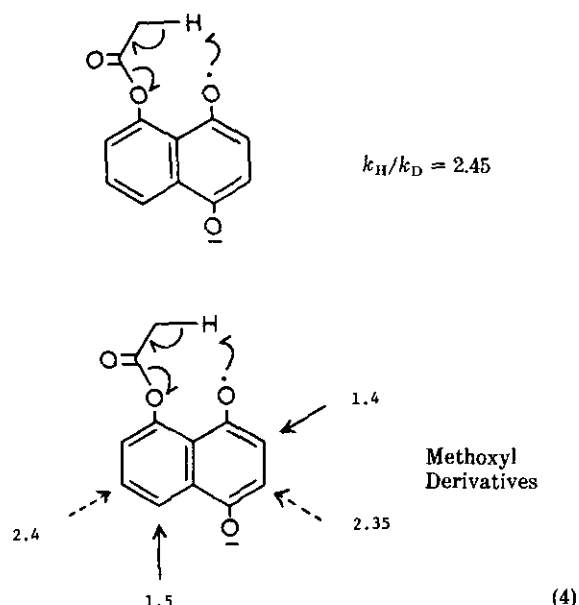
state, the reaction will become more "product-like" (*18*), and the kinetic isotope effect will be smaller than that observed for the unsubstituted compound (*15*). A methoxyl group placed at either the 3- or 6-positions [see Eq. (3)] should have no effect on the radical center at position 1, and should thus not alter the isotope effect to any extent.

$$k_H/k_D = 2.45$$

Methoxyl
Derivatives

(4)

The results of this experiment are shown in Eq. (4). The isotope effect for compounds substituted at positions 2 and 5 are dramatically lowered, whereas those for the 3- and 6-substituted isomers are little affected when compared with the isotope effect of 2.45 noted for the parent compound. This suggests the possibility that in this case, the reaction is occurring by a radical mechanism.

Collisional Processes of Negative Ions

Let us now consider a different type of negative ion reaction. In a conventional mass spectrometer, a nondecomposing negative ion is accelerated to a high translational energy (typically 2,000 to 10,000 eV, depending upon the spectrometer) as it leaves the ion source. If this accelerated negative ion suffers a collision with a nonreactive neutral molecule, there is a probability that some of the translational energy of the ion will be converted into internal (mainly electronic and vibrational) energy. If this occurs, the negative ion must liber-

ate excess internal energy by one of a number of processes, viz collisional deactivation, autoionization, a radiative process, or by some type of fragmentation.

It has known for over a decade that positive ions undergo fragmentation after collision with a neutral molecule (*20, 21*). This process, called collisional activation, is arguably more important for negative ions (*22*), since such species, unlike positive ions, often do not have sufficient energy to allow any decomposition. Negative ions can therfore be forced to fragment by collisional activation. For example, a negative ion derived from a molecule containing an amide bond will only cleave at the N-C bond after collisional activation (*23*).

Of more theoretical and applied use are those collision processes which induced a change in the charged state of a negative ion. The pioneering work of Cooks and Beynon (*7*) on collision processes of positive ions was well underway when we commenced our work on the charge stripping of negative ions. We have shown that any negative ion may be converted into a decomposing positive ion by the reaction $A^- + N \rightarrow A^+ + N + 2e^-$. The energy required to form a stable parent ion A^+ is equal to the sum of the electron affinity of A and the ionization energy of A. Normally, ions A^+,

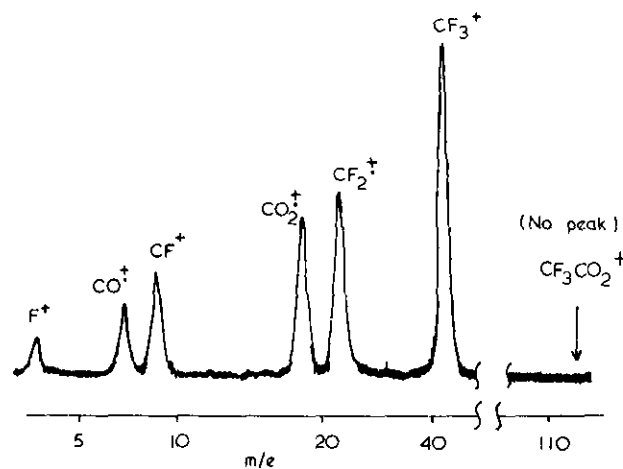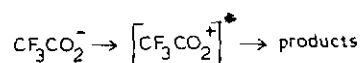$$CF_3CO_2^- \rightarrow \left[CF_3CO_2^+\right]^* \rightarrow products$$

FIGURE 3. Dissociative charge inversion spectrum derived from the $CF_3CO_2^-$ ion of $(CF_3CO)_2O$. Hitachi Perkin Elmer R.M.U. 6D mass spectrometer, electron energy 70 eV, accelerating voltage -3.6 kV, sample pressure 2×10^{-6} torr in the source, and collision gas (N_2) pressure of 1×10^{-5} torr in the second field-free region. Decompositions occurring in the second field-free region. Electric sector set to transmit main beam of negative ions, magnet transmits positive ions, spectrum produced by magnetic field scan.
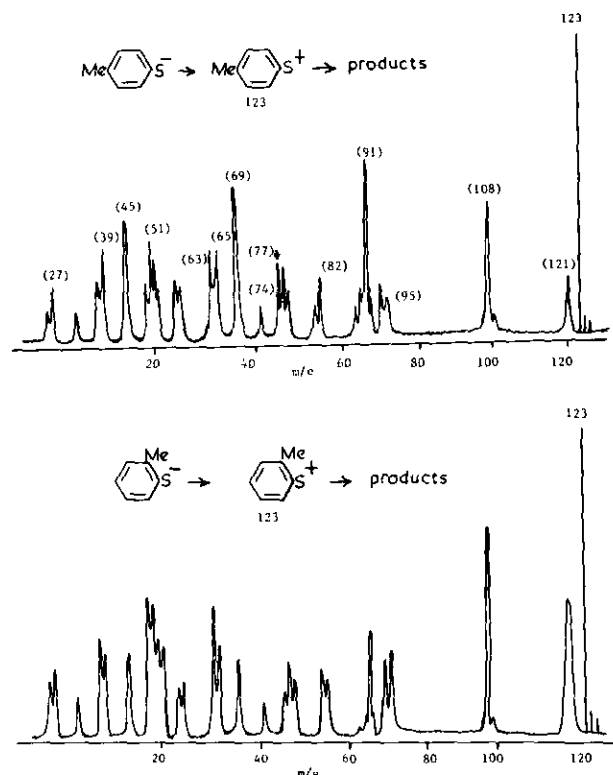
FIGURE 4. Dissociate charge inversion spectra of (a) *p*-MeC$_6$H$_4$S⁻ from (*p*-MeC$_6$H$_4$S)$_2$ and (b) *o*-MeC$_6$H$_4$S⁻ from (*o*—MeC$_6$H$_4$S)$_2$. Experimental conditions as recorded in the legend to Figure 3. Peaks are shown with the conventional masses in brackets.

charge-inversion spectrum of any negative ion gives a fingerprint for the parent positive ion, since this spectrum, at a given accelerating potential, is independent of the pressure of the collision gas provided the pressure in the collision region is less than 3 × 10⁻⁵ torr (*26*). As an illustration of this feature, the *o*- and *p*-isomers of MeC$_6$H$_4$S⁻ give reproducible, but different charge inversion spectra (*26*) (see Fig. 4).

A charge inversion spectrum of a negative ion can also give structural information about that negative ion, provided the anion does not undergo rearrangement during the collision process, and provided that the parent positive ion does not rearrange prior to fragmentation. Fortunately, cases of positive ion rearrangements of this type seem to be relatively rare, and we estimate that fragmentation takes place within 10⁻⁸sec of the collision process (*26*). Let us consider a particular example where a charge inversion spectrum confirms the structure of a negative ion produced by a rearrangement process. The negative-ion mass spectrum of *o*-nitrophenyl benzoate (Fig. 5) shows a base peak at *m/e* 121 which is thought to correspond to the benzoate negative ion PhCO$_2$⁻ (see Fig. 5). The charge inversion spectrum of *m/e* 121 from this system was compared with that of authentic PhCO$_2$⁻ produced from benzoic anhydride. The two spectra were identical, thus confirming the structure of the rearrangement ion (*29*).

formed within 10⁻¹²sec, of the collision process are generally not stable, and peaks due to these species are either not detected, or alternatively are observed in small abundance. Ions A⁺ are generally formed in electronically excited states, and fragment in less than 10⁻⁸sec to produce an intense spectrum of fragment positive ions (*24-28*). Fragmentations can be measured in either field-free region, but better resolution is achieved using the second field-free region. In this experiment the electric sector transmits negative ions, the collision process occurs in the second field-free region, and the magnet is set to accept positive ions. Typical spectra are shown in Figures 3 and 4.

The dissociative charge inversion spectrum of a negative ion has a number of applications. Fragment negative ions often have no positive ion analog produced by conventional ionization. The formation of positive ions by charge inversion thus permits the study of species not available by other methods. A particular example of this is the perfluoroacetate cation (see Fig. 3). Second, the

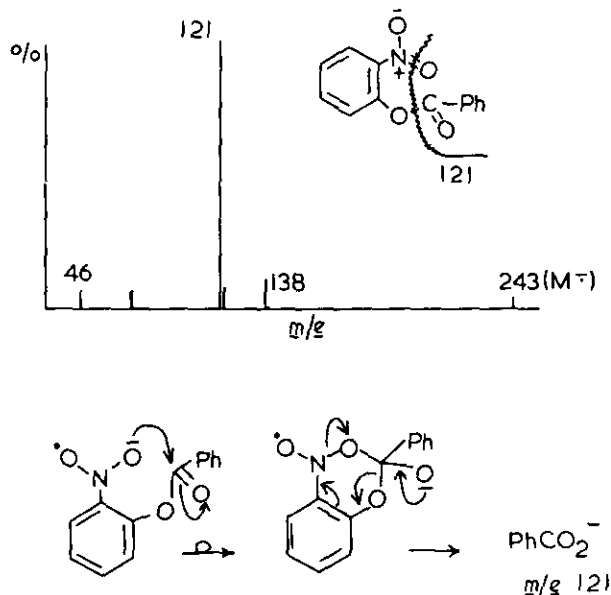FIGURE 5. Negative ion mass spectrum of *o*-nitrophenyl benzoate. Experimental conditions: 70 eV, source prssure 2 ×10⁻⁶ torr, accelerating potential −3.6 kV.

Finally, the charge inversion spectrum of a negative ion may also be used as an aid for the structure determination of unknown molecules. A molecule may sometimes form a molecular anion (by secondary-electron capture), or an M − 1 ion [by HO⁻/NICI (30)], which does not fragment. Alternatively, a compound which does not yield negative ions may form a stable molecular negative ion when an electron capture group [e.g. nitrophenyl (31) or perfluorophenyl (32)] is specifically built into that molecule. Structural information from fragmentation data is not available in any of these cases. Measurement of the collision induced charge inversion spectrum of the molecular negative ion [or $(M - 1)^-$ ion when appropriate] gives the required structural information. Experimentally all that needs to be done is to measure the negative ion spectrum to give the molecular weight, introduce nitrogen into the collision region, and reverse the polarity of the magnet to allow the measurement of positive ions. This technique, which constitutes an effective marriage of negative and positive ion mass spectrometry, has been applied to amino acids and peptides (33), and to the NICI spectra of mixtures of organic compounds (34). A particular example of the method is shown for a dipeptide derivative in Figure 6. The negative ion spectrum is dominated by the molecular negative ion; the charge inversion spectrum determines the structural features.

The study of the gas phase chemistry of polyatomic negative ions is still in its initial stages. Until a few years ago only a handful of research groups were active in this area. The advent of NICI mass spectrometry has seen a surge in interest into the applications of negative ion mass spectrometry. Negative ion facilities are gener-

ally available with the latest generation of mass spectrometers: hopefully this will lead to the widespread acceptance of negative ion mass spectrometry as a viable analytical technique.

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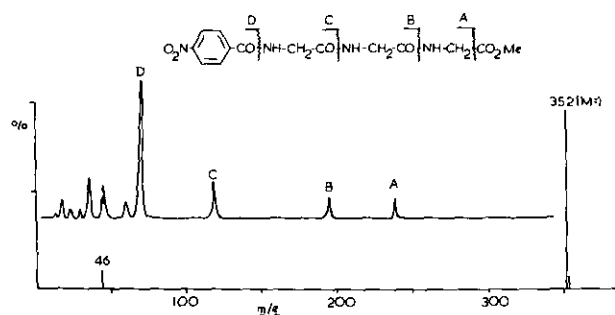
FIGURE 6. Lower trace. Negative ion mass spectrum. Experimental conditions as recorded in the legend to Fig. 5. Upper trace. Dissociative charge inversion spectrum derived from the molecular negative ion. Experimental conditions as recorded in the legend to Fig. 3.

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